Discussion of "Electrochemical Investigations of Alkali-Metal Intercalation Reactions in TiS2: Chronoamperometric Determination of Mass and Charge Transport Properties of Liquid Electrolyte Systems" [Anthony Vaccaro, T. Palanisamy, R. L. Kerr, and J. T. Maloy (pp. 682–688, Vol. 129, No. 4)]

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that McCann and Badwal rationalize their findings in terms of an infinite network of serial RC elements connected parallely, i.e., $\begin{matrix} R—R\ldots—R—\cdot \\ | \quad | \quad\quad | \\ C—C\ldots—C—\cdot \end{matrix}$. Both R's and C's are taken as obeying an exponential distribution.

We wish to point out that even though the endeavor of these authors appears to be successful it is certainly not unique. We were able to prove, for example, that a power function distribution of R's and C's also results in a CPAI of the required functional form. Let the k-th elements of the network be given as $R_k = R_0N(N/k)^\beta$ and $C_k = (C_0/N)(N/k)^\alpha$ where N is the number of elements in the series. If one writes the admittance as $Y_T = \sum_{k=1}^{N} i\omega C_k/(1 + i\omega C_k R_k)$ and makes N to converge to infinity the sum for Y_T transforms into an integral which can be evaluated as

$$Y_T = (i\omega)^\gamma R_0^{\gamma-1} C_0^\gamma \frac{\pi}{(\alpha+\beta)\sin(\gamma\pi)}$$

where $\alpha + \beta > \beta + 1 > 0$, and $\gamma = (1 + \beta)/(\alpha + \beta)$. Hence any pair of power functions for the distributions of R's C's, respectively, results in a CPAI (with the sole limitation $\alpha + \beta > 1 + \beta > 0$).

This shows that it is dangerous to assign any physical meaning to elements of an infinite equivalent circuit. Our view is that a CPAI should be regarded as a single element, the infinite network being only a remote electrical analogy. The ccurrence of a CPAI may also indicate some dispersion in a transport process, *e.g.*, waiting time distribution of diffusive jumps which leads to a frequency-dependent diffusion coefficient in amorphous semiconductors;[80] there seems to be, however, no direct relationship between such a dispersion and the distribution of the R and C elements discussed above.

The Mott-Schottky equation contains the differential capacitance of the semiconductor depletion layer, and not the measured total cell or electrode capacitance. These are equal only if the equivalent circuit of the electrode is a simple serial RC combination, which is carefully and convincingly demonstrated in the paper not to be the case. The frequency dependent Mott-Schottky slope (Eq. [26] and Fig. 12) is therefore simply an artifact, as is often the case.[81]

Although there is little point in discussing the physical meaning of the infinite RC networks, as we have demonstrated in paragraph one, a further comment needs to be made concerning the erroneous deviation of the CPAI from the distributions of Eq. [7]-[10]. This is best illustrated by the fact that the resultant admittance has the wrong dimension [energy/impedance]. This can be traced back to the (implicit) assumption that any "activation energy" E between zero and infinity is equally probable, which means that E has a nonphysical, non-normalizable distribution.

J. F. McCann[82] and S P. S. Badwal:[83] Nyikos and Pajkossy have correctly commented that the present model which includes the assumptions of exponential distributions of R and C elements is nonunique and that an infinite network is but a remote electrical analogy. It is clear, that until exhaustive experimental and corresponding theoretical studies of impedance over very wide frequency ranges and with instruments capable of giving high resolution, low noise measurements have been performed for a large number of semiconductor/electrolyte systems, that any theoretical or physical interpretation of the frequency dependent impedance, for such systems, should be regarded as being extremely tentative. This latter point is made strongly in the present paper and, in our view, the useful comments offered by Nyikos and Pajkossy in this regard, reinforce the theme of the present publication.

We should clarify that while the frequency dependent Eq. [26] is referred to as a frequency dependent Mott-Schottky relation it is not a modified Mott-Schottky equation. Equation [26] is an empirically observed relation which was first discussed in detail by Dutoit *et al.*[84] Since the measured capacitance is often frequency dependent and since the origin of the frequency dependent capacitance is presently not known, then it follows that it is correct to define the measured capacitance, C, (Eq. [26]) as the cell capacitance rather than as the capacitance of the depletion layer. The Mott-Schottky relation is correctly given by Eq. [1] in the paper and the fact that this relationship is only strictly applicable when the equivalent circuit is a simple nonfrequency dependent series RC network is clearly stated in the introduction.

Gomes and Cardon in their present comments have pointed out, that in their view, the explanation of the frequency dependent 1/C2 *vs.* V behavior is a frequency dependent dielectric constant. While this view appears to be a reasonable one, and also one that can be to some extent theoretically supported, we are of the opinion, that due to the large number of possibilities, this interpretation may well prove to be oversimplistic, particularly since semiconductor/electrolyte and semiconductor/metal interfaces have complex structures, which can, from a theoretical view point, at least, significantly contribute to the measured impedance of a system.

A syntax error in the paper has been pointed out by Nyikos and Pajkossy. E is correctly defined as a dimensionless function. Dimensional consistency is maintained by the dimensions assigned to α and β although kT can be eliminated from Eq. [7] and [8] so that in this case α and β do not assume dimensions.

Electrochemical Investigations of Alkali-Metal Intercalation Reactions in TiS_2: Chronoamperometric Determination of Mass and Charge Transport Properties of Liquid Electrolyte Systems

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(pp. 682-688, Vol. 129, No. 4)

K. West, S. Atlung, and T. Jacobsen:[85] The data reported in the above paper for solid-state diffusion of Li^+ in TiS_2 and the kinetics for the charge transport by Li^+ across the TiS_2/organic electrolyte interface do not agree with data we have found for the same system with propylene carbonate (PC) as electrolyte solvent. Also we disagree with the conclusion drawn by the authors that slow charge transfer kinetics contribute significantly to the behavior of the cathode used in Li/organic electrolyte/TiS_2-batteries.

To illustrate our point, the accompanying Fig. 1 and 2[86] depict the chemical diffusion coefficient of lithium in Li_xTiS_2 ($\tilde{D}_{Li}$) and the charge transfer resistance between $LiClO_4$/PC electrolyte and Li_xTiS_2 (Rt) as measured by a-c impedance on one crystal face of a TiS_2 single crystal perpendicular to the c-axis.

First our results are that $\tilde{D}_{Li}$ varies one to two orders of magnitude with composition, showing a broad

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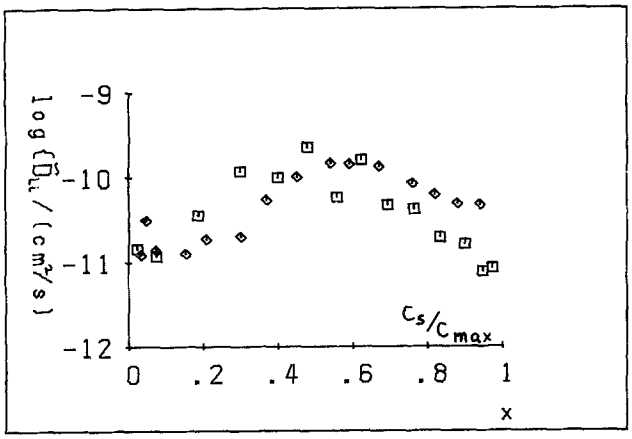

Fig. 1. Chemical solid-state diffusion coefficient for Li^+ in TiS_2. Electrolyte 1m $LiClO_4$ in PC. Two independent experiments.

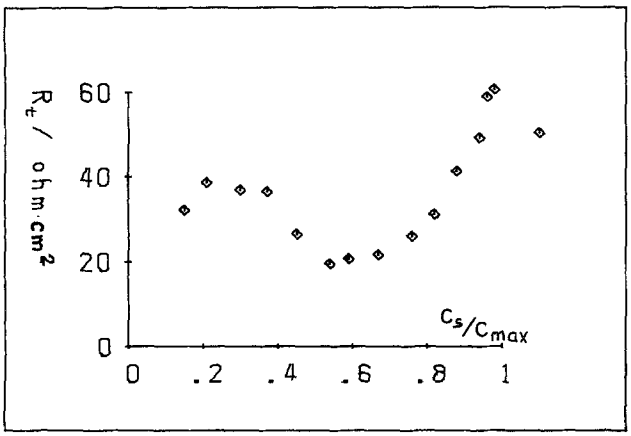

Fig. 2. Charge transfer resistance ($di/d\epsilon$, $\epsilon = \epsilon_{eq}$) for Li^+/TiS_2 electrolyte as Fig. 1.

maximum near $X = 0.5$. This is in agreement with NMR-relaxation measurements.[87] We also observed diffusion coefficients considerably lower than cited in the paper.

The methods used by the authors for determination of $\tilde{D}$ are based on an estimate of the time constant l^2/D determined from the transition region between semi-infinite diffusion ($t^{-1/2}$-law) and diffusion in a bounded region. We fully agree with the authors, that determination of time constants is the best way of characterizing diffusion in powders, avoiding the problems with determination of true surface area, and with sorting out effects due to coupling between electrolyte transport and transport in the electrode. Converting time constants to diffusion coefficients is, however, not straight forward and requires careful consideration of the following points: (*i*) The average dimensions of single particles (not agglomerates) must be well characterized. Using "well conditioned" electrodes, *i.e.*, electrodes cycled several times, requires determination of particle size on used electrode powders as these disintegrate upon cycling. (*ii*) The geometry of the particles must be known. Using expressions derived for plane geometry instead of, *e.g.*, cylindrical geometry, which is most adequate for two dimensional conductors as TiS_2, overestimates the diffusion coefficients by a factor ~3.8. (*iii*) Time constants are often measured with large differences between surface and bulk concentration in the electrode particles, and thus only yield an overall diffusion coefficient, close to the maximum diffusion coefficient in the interval considered.

[87] C. Berthier, "Fast Ion Transport in Solids," Vashista, Mundes, Shenoy, Editors, p. 171 (1979).

As for the estimates of the charge transfer kinetics, it is our opinion that the analysis of the experimental data is invalid, as the expressions derived by the authors are based on the following erroneous assumptions: (*i*) The authors expression [3] is derived for the case of equilibrium at the electrode electrolyte interface (cf., *e.g.*, Footnote [88], pp. 50-51). It is therefore inconsistent with the authors conclusions about the significant kinetic overvoltage to use this equation in the development of their Eq. [4]. The correct expression is (Footnote [88], pp. 74-77)

$$|i| = nF\vec{k}(\epsilon)(c_m - c_b)\exp\xi^2 \operatorname{erf}\xi \qquad [1^*]$$

where $\xi = t^{1/2}(\vec{k}(\epsilon) + \overleftarrow{k}(\epsilon))/D^{1/2}$ and Delahay (*loc. cit.*) has shown that for $\xi < 0.1$ the current found from [1*] is only a small fraction of the current calculated according to [3]. In Table I the authors indicate $\xi \simeq 0.02$ or smaller for their measurements. (*ii*) A kinetic expression of the form of [4] is only valid if the equilibrium potential obeys a Nernst equation as apparently presumed by the authors

$$\epsilon_{eq} = \epsilon^\theta + \frac{RT}{F}\ln\frac{c_o}{c_s} \qquad [2^*]$$

Equation [2*] predicts a potential variation for a 90% utilization of *ca.* 70 mV whereas for TiS_2 the corresponding variation is *ca.* 480 mV. This is expressed by the potential relation proposed by Armand[89] which for a constant c is

$$\epsilon_{eq} = \epsilon^\theta(c) + \frac{RT}{F}\left(\ln\frac{c_m - c_s}{c_s} - f\frac{c_s}{c_m}\right) \qquad [3^*]$$

For $i = 0$ a kinetic expression must give a solution for the potential which is identical with the thermodynamic equilibrium condition. The authors Eq. [4] renders for $i = 0$ an expression equivalent to [2*] which is in large disagreement with the measured potential[90] and with [3*] ($f = 16$) as shown on Fig. 3.

A consistent kinetic expression could have the form

$$i = F(\vec{k}(\epsilon)c_s/c_m - \overleftarrow{k}(\epsilon)(c_m - c_s)\cdot c/c_m) \qquad [4^*]$$

[88] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York (1954).
[89] M. Armand, Dissertation. Grenoble (1978).
[90] A. H. Thompson, *This Journal*, 126, 608 (1979). See also T. Jacobsen *et al.*, *Electrochim. Acta*, 27, 1007 (1982).

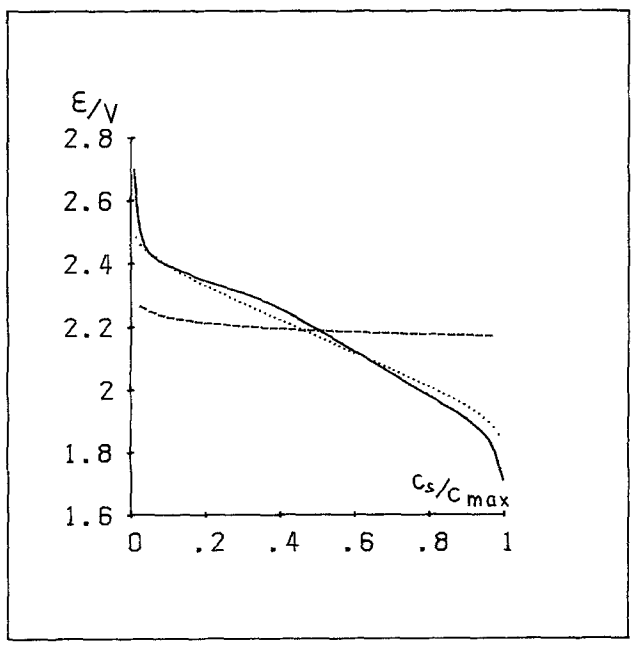

Fig. 3. Equilibrium potential for TiS_2 for $c_{Li^+} = c^\theta$. —— Measured in electrolyte as Fig. 1. . . . . Calculated from [3*]. $f = 16.2$. ----- Nernst dependence as assumed by Vaccaro *et al.* in [4].

where the k's are potential dependent rate constants (cf. [1*]) fulfilling the condition that the equation

$$\frac{\overleftarrow{k(\lambda)}}{\overrightarrow{k(\lambda)}} = \frac{c_m}{c_m - c_s} \cdot c \qquad [4]$$

for all values of c, c_s, and c_m must give $\lambda \equiv \epsilon_{eq}$ from [3*]. The Volmer-Butler type of expression used by the authors fails to fulfill these conditions.

From the reasons outlined above, we cannot accept the conclusions reached by the authors concerning the significance of influence of charge transfer kinetics on the TiS_2 overvoltage. To illustrate this point, we find from the values for the charge transfer resistance given in Fig. 2, using 50 ohms cm^2 as an upper limit, that for a 5 μm TiS_2 particle discharged at a current corresponding to a 4 hr discharge, the charge transfer overvoltage should not exceed 1.5 mV.

J. T. Maloy:[91] We appreciate the interest of these readers and the submission of their data indicating that the lithium diffusion coefficient in TiS_2 varies with the stoichiometry of the solid-state material. This is not an unreasonable possibility. Unfortunately, data of the kind presented do not prove that this is the case: differences in impedance measurements carried out on separate chemically-prepared samples of different composition could be ascribed to sample-to-sample variations in crystal microstructure, contact resistance, liquid junction potential, etc. These variations no doubt contribute to the scatter in the data submitted by these investigators.

To settle this issue properly, the effect of the variation of the diffusion coefficient with chemical composition should be treated theoretically for the electrolysis of a single crystal of TiS_2 to $LiTiS_2$ and this model should be subjected to experimental verification. This model would require, for example, that Fick's first law be written

$$-J(x,t) = D(x,t)\frac{\partial C(x,t)}{\partial x} \qquad [1']$$

where $D(x,t)$ would depend upon $C(x,t)$ in a manner described, to a first approximation, by the data presented in the commentary to our paper. Fick's second law would have to be modified accordingly. This is an interesting boundary value problem which, to our knowledge, has not been solved rigorously. We are presently trying to model this behavior using digital simulation techniques[92] and, if these provide any new insights to this problem, they will become the subject of a future communication. Contrary to West *et al.*, we feel that the "overall" diffusion coefficient would lie closer to the minimum D within the interval instead of the maximum.

We agree completely with these readers that the determination of the diffusion length l is the most ambiguous part of our method for measuring D. Particles of the same size should have been used to prepare an electrode and, as this commentary points out, these particles should have been measured again after cycling. If one assumes, however, that cycling results in the formation of only smaller particles through crystal exfoliation, our preliminary work provides an estimate of the maximum value of D because it is based on the maximum value of l. This should have been stated in the original paper.

We disagree with West *et al.*, concerning the equilibrium requirement for Eq. [3]. The only requirement for the validity of [3] is that C_s be constant. While this can result from equilibrium, it can also be the result of a steady-state process. In the case of charge transfer kinetics, for example, a constant interfacial concentration is obtained when the rate of charge transfer equals the rate of mass transport.

We considered a current-time equation similar to [1*] when we first took up this problem. The expression we used (taken from [93], p. 166, or [94] p. 74) gives the complete solution to the boundary value problem solved by Delahay

$$i(t) = n\mathbf{F}Ak_f(E)C \exp \xi^2 \operatorname{erfc} \xi \qquad [2']$$

where

$$\xi = \left[\frac{k_f(E)}{D_o^{1/2}} + \frac{k_b(E)}{D_R^{1/2}}\right] t^{1/2} \qquad [3']$$

Note that C and D_o refer to fluid solution parameters, whereas D_R represents a solid-state parameter; this distinction is not drawn in [1*]. By expanding erfc ξ in the manner suggested by Delahay (see [94], p. 74), one may obtain the long time ($\xi > 3$) expression

$$i(t) = \frac{n\mathbf{F}ACD_R^{1/2}}{\pi^{1/2}t^{1/2}}\left[\left(\frac{D_R}{D_o}\right)^{1/2} + \frac{k_b(E)}{k_f(E)}\right]^{-1} \qquad [4']$$

which would have to be valid if [2'] and [3'] (the correct form of [1*]) provide the "correct expression" for [4]. At negative potentials $k_f(E) >> k_b(E)$ and [4'] becomes

$$i(t) = \frac{n\mathbf{F}ACD_o^{1/2}}{\pi^{1/2}t^{1/2}} \qquad [5]$$

That is, at high overvoltages, the rate of the electrointercalation reaction is determined entirely by fluid solution parameters; it is independent of the rate of solid-state diffusion. Of course, this is contrary to experimental observation.

The reason for this discrepancy is obvious: the boundary value problem correctly solved by Delahay is not the boundary value problem for electrointercalation. Equation [2'] is obtained by assuming that the product of the electrode reaction undergoes semi-infinite linear diffusion within the same medium as the reactant which produces it and that its interfacial concentration may increase without limit if $D_R < D_o$ and if $k_f(E) > k_b(E)$; in electrointercalation, the intercalated product undergoes finite diffusion in a different medium and its maximum interfacial concentration is determined by the maximum stoichiometry of $LiTiS_2$. In fact, this interfacial product concentration controls the rate of the forward reaction to some extent: when the maximum interfacial product concentration is achieved at a given potential, the forward reaction must cease, regardless of the forward rate constant at that potential.

This having been observed, we had three choices: (*i*) solve this new boundary value problem rigorously or numerically; (*ii*) change the meaning of some of the parameters in [2'] and hope that it would work; (*iii*) assume that Butler-Volmer kinetics are operative in electrointercalation and use our diffusion equations [2] and [3] to estimate interfacial concentrations in the mass-transport limited form of the current-overpotential equation (see[93] p. 102) in an attempt to estimate the rate parameters. West *et al.* would have had us elect either the first or second choice, as they apparently did. Because we had a substantial amount of experimental data indicating that mass-transport limited current behavior was achieved over a 500 mV range, we elected the third choice: we wanted to call prompt attention to the fact that charge transfer kinetics could be responsible for this behavior. (Prior to our work, charge transfer kinetics were not considered in studies of these materials.) While the method we chose is not nearly as elegant as an exact solution, it is expedient and valid to the extent that Butler-Volmer kinetics are operative.

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